Perspective

Chemical Diversity of Zeolite Catalytic Sites

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Introduction

The past decade has witnessed important progress in our understanding of catalytic reactions in zeolite materials to the point that in many cases we know with confidence the chemical bonds that form and break as reactants are converted into products. This reflects advances in spectroscopic techniques-IR, NMR (Hunger and Wang, 2006),[1] X-ray spectroscopy, etc., extensive use of *in situ* characterization methods, sophisticated use of computational chemistry (Rozanska et al., 2005),[2] and tremendous success in the synthesis and characterization of new materials. In this perspective, I describe selected examples of progress in zeolite catalysis that illustrate how our ability to elucidate in molecular detail the structure of the catalytic site and its surroundings can be used to understand activity and selectivity. These examples illustrate trends in zeolite catalysis research that are likely to be important in the future development of novel and practical catalysts. The new catalysts represent exciting opportunities for chemical engineers to improve on existing processes, reduce the environmental impact of current technologies, and develop completely new processes for the manufacture of molecules of value to our society.

Background

Zeolites are microporous materials built by linking in a periodic pattern four connected oxide tetrahedra. The framework structure of zeolites has pores and cavities that enclose ions and adsorbed molecules, both of which have considerable freedom of movement permitting ion exchange and reversible adsorption and desorption (see Figure 1). In the center of the tetrahedra are atoms with low electronegativities (Si^{IV}, Al^{III}, Ge^{IV}, Fe^{III}, etc.), and in the corners are oxygen anions (O^{2-}). The tetrahedra ($[SiO_4]$, $[AlO_4]^-$, etc.) are connected forming more complex units—such as rings and cages—including pores and pore networks that extend throughout the zeolite crystal. The rings controlling the dimensions of the molecules that are adsorbed in zeolites are usually formed of 8-, 10- or 12-tetrahedral units, although zeolites with up to 18-ring pores (and odd-numbered-rings) have been synthesized (Corma et al., 2006).[3] Zeolites with 8-tetrahedral ring pores are known as small-pore zeolites, and have effective pore diameters of about 4 Å (similar to the diameter of dinitrogen or linear alkanes). Zeolites with 10-ring pores have effective pore diameters of about 5.6 Å allowing molecules, such as toluene or small branched hydrocarbons (e.g., 2-methylbutane), to travel through the pore system. 12-ring pore zeolites are known as large-pore zeolites, and have effective pore diameters of about 7.5 Å. Molecules such as hexamethylbenzene can diffuse in most large-pore zeolites. In industrial catalysis zeolites with 10-ring and 12-ring pores are the materials most frequently used.

A zeolite formed only of $[SiO_4]$ tetrahedra has no active sites, and is not an attractive catalyst; the catalytic activity is the result of the substitution of heteroatoms in the framework. Most frequently the silicon atoms are substituted by trivalent metal atoms (Al^{III}, B^{III}, Fe^{III}, Ga^{III}, and others) forming negatively charged tetrahedra (i.e., $[AlO_4]^-$). The negative charge is balanced by an extra-framework cation (Na^+, Ca^{2+}, etc.), and if the cation is a proton, the zeolite becomes a solid acid. Framework substitution by tetravalent metal-atoms (Ge^{IV}, Ti^{IV}, Sn^{IV}, Zr^{IV}) is also widely used to provide Lewis acid sites within the zeolite pores. Furthermore, if the negatively charged framework sites are balanced by a cation with the ability to change oxidation state, it is possible to facilitate redox catalysis through the extra-framework cations. The catalytic potential of these alternatives is discussed in more detail in the following.

Classical Brønsted Acid Catalysis

As a group, zeolites are the most important solid acids used in the chemical industry (Tanabe and Holderich, 1999).[4] For instance, about 40% of the gasoline used worldwide is produced from the cracking of the heavier fractions of petroleum on fluidized catalytic cracking catalysts containing zeolite Y as the main ingredient (Corma, 1995).[5] Most of the ethylbenzene (precursor to polystyrene), cumene (precursor to acetone and phenol), xylenes (precursors to polyesters like PET) are produced over acid zeolites of different structures and

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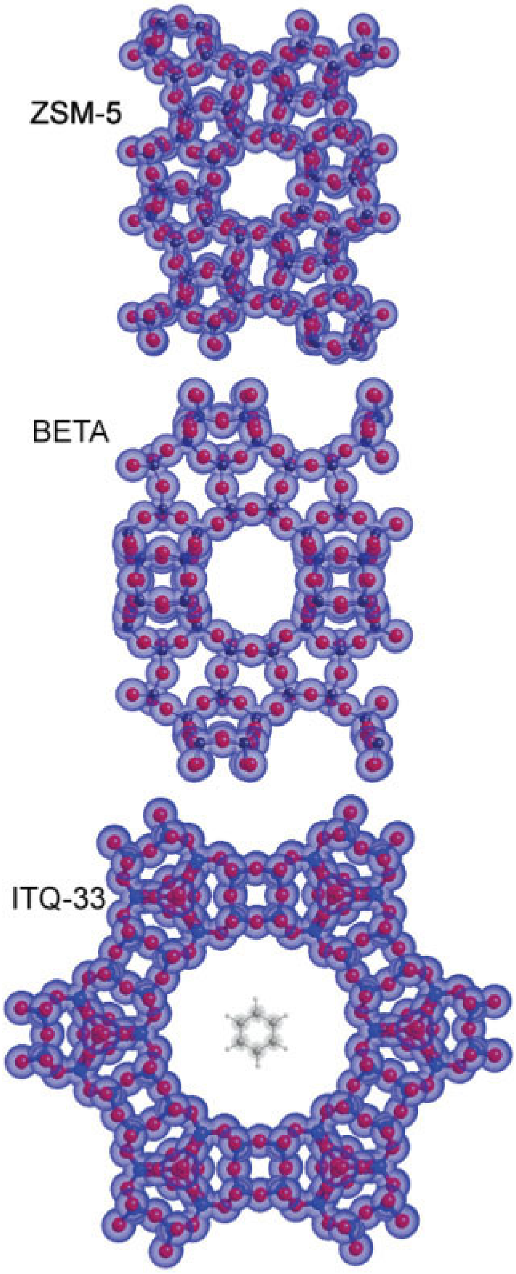

Figure 1. Structure of three zeolites.

Zeolite ZSM-5 (top) has a 10-ring pore system. Zeolite beta (middle) has a 12-ring pore system and zeolite ITQ-33 (bottom) is a new extra-large pore zeolite with a 18-ring pore system. In the middle of the pore of ITQ-33 a molecule of benzene is depicted to give a sense of scale.

compositions. These reactions are conducted over zeolites containing Brønsted acid sites, that in the most simple form can be described as a hydroxide group bridged between an aluminum, and a silicon atom Si-OH-Al (Corma, 1995).[5] The bridging oxygen atom has three bonds, and since formally the oxygen atom has a bond order of two, these bonds are relatively weak. In particular, the weak OH bond allows for a facile donation of the proton H^+ to an adsorbed molecule, and can be thought of as the origin of the acid strength of zeolites.

There are three possible outcomes of the interaction of an adsorbed molecule with a zeolite Brønsted acid site (Corma and Orchilles, 2000; Zecchina et al., 2005)[6,7]:

1. Formation of a hydrogen bond complex between the adsorbed molecule, and the proton of the acid site. This is observed when the gas-phase proton affinity of the adsorbate is low (usually below 858 kJ/mol, as is the case with CO or methane). This is an example of physisorption as no bonds are broken or formed, and the heat released upon adsorption is small.

2. Complete donation of the proton to the adsorbed molecule and charge separation with a negative charge on the $[AlO_4]$ tetrahedron and a cationic adsorbed species. This is observed for adsorbates with proton affinities larger than $\sim$858 kJ/mol, such as ammonia or dimethylbenzenes that form ammonium (Gorte, 1999)[8] and the dimethylbenzylium cations (Bjorgen et al., 2005)[9] upon adsorption on acid sites, respectively. This is evidently a form of chemisorption.

3. Formation of a surface species covalently bound (via a framework oxygen atom) to the zeolite. A classical example of such surface intermediates is the ethoxide group formed by the reaction of ethylene with the acid site. These surface species are usually very reactive and can isomerize/desorb rapidly. In catalytic reactions, the surfaces species are de facto reaction intermediates (Corma and Orchilles, 2000).[6]

It is important to know which type of interaction is dominant as this determines much of the chemistry that will follow. Figure 2 (I-III) shows three structures of ethylene adsorption on an acid site (Kazansky et al., 2006).[10]

An example of the aforementioned case 1 is structure I, showing a *hydrogen bonded complex* of ethylene with the acid site. Structure III shows the results of the *reaction* of the ethylene with the acid site, where an ethoxide surface species is formed (case 3). At low-temperatures structure I is stable, but even at room-temperature the surface ethoxide group is easily formed. Both complexes have been investigated by IR spectroscopy (Kazansky et al., 2006; Kondo et al., 2005),[10,11] and recently the ethoxide has been identified also using NMR spectroscopy (Jiang et al., 2006).[12] The structure II illustrates the geometry of the transition state, and shows—what is now generally accepted, but was not until the 90s—that transition states on zeolites are carbenium-ion-like. In this particular case carbon C_b is nearly planar as expected for a primary carbenium ion. An important characteristic illustrated in Figure 2 is that the active site of acid zeolites is really bifunctional, and it is better described as Lewis-base-assisted Brønsted acid catalysis. Not only is the proton participating in the reaction, the oxygen coordinated to the aluminum opposite to the acid sites also plays a crucial role in stabilizing the transition state. In fact, the product of this elementary reaction step is bonded to this oxygen, not to the one with the acid proton. This concerted action by the acid and basic function of the site is a process observed over and over in zeolite acid catalysis, and is a characteristic hardly emphasized enough in the open literature.

Alkoxide intermediates (such as III) are more stable than carbenium ions for primary and secondary carbons, such as ethoxide and isopropoxide. However, the energetic difference between the alkoxide and the carbenium ion is comparable for tertiary carbons, leading to a dynamic equilibrium between the two surface intermediates (Tuma and Sauer, 2005).[13] These structures shuttle constantly between the alkoxide and the ion

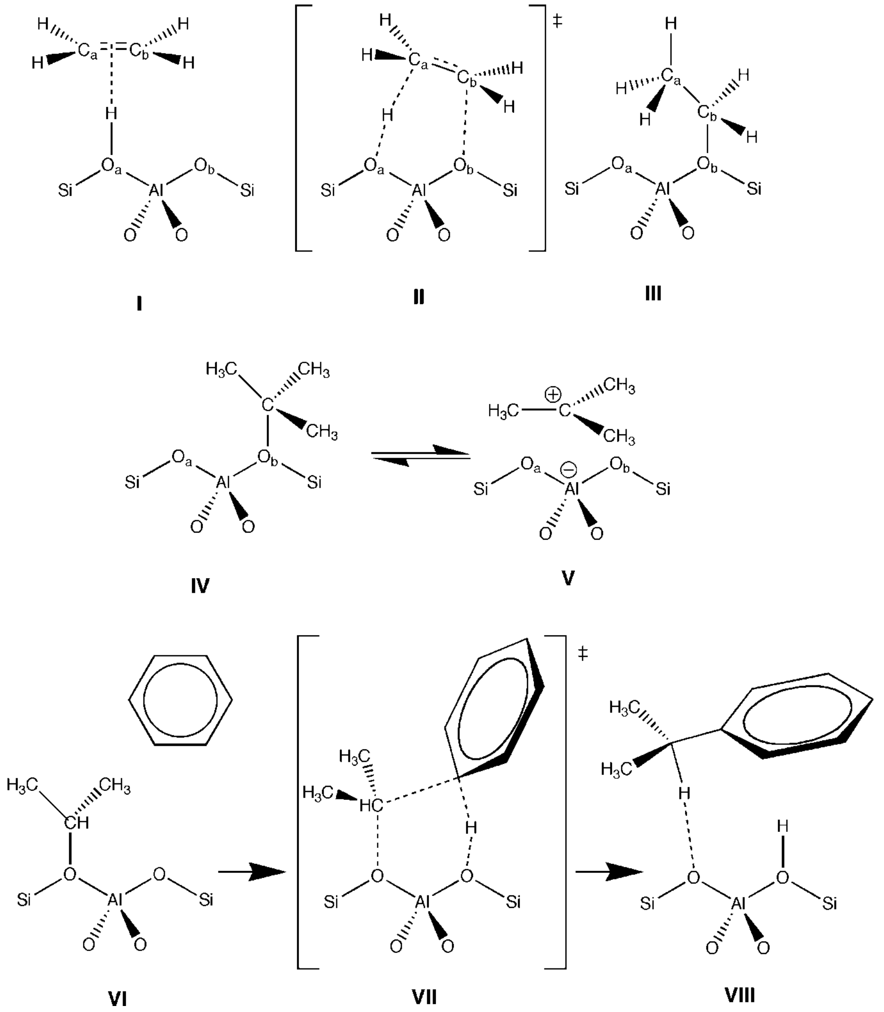

Figure 2. Examples of coordination complexes formed by adsorption of a base on a Brønsted acid site (I-V) and carbon-carbon bond formation via surface alkoxide species (VI-VIII).

(case 2). Calculations show that the alkoxide (IV), or the carbenium ion (V), can be the most stable species depending on the specific site investigated, and the energetic difference between the two intermediates is just a few kcal/mol.

Both alkoxide (IV), and carbenium ion (V) intermediates are highly reactive, and can form new carbon-carbon bonds with organic molecules physisorbed inside the zeolite pores. An important industrial reaction conducted over zeolites is the synthesis of cumene from propene and benzene (Rozanska et al., 2005).[2] It has been reported that the kinetically relevant pathway for the formation of cumene is a sequential reaction in which propene reacts with a Brønsted acid site to form an isopropoxide intermediate. This isopropoxide intermediate (VI), then reacts with a benzene molecule to form cumene and regenerate the Brønsted acid site (see VIII in Figure 2).

This bimolecular reaction has been investigated extensively, and recent studies have shown that the stability of the transition state (VIII), greatly depends not only on the stabilization effect of the acid site, but also on the stability provided by the surrounding zeolite pore structure to the bulky intermediate (Rozanska et al., 2005).[2] Structure VIII again shows the bifunctional role of the zeolite acid sites, and the participation of oxygen atoms that are not bonded to the alkoxide intermediate. Other C-C bond forming reactions (such as ethylene dimerization to form n-butenes) proceed in a similar fashion (Namuangruk et al., 2005).[14]

Methoxy species in zeolites deserve a separate discussion as they cannot be formed from alkenes, and they show very interesting reactivity toward a wide variety of molecules (Jiang et al., 2006).[12] Methoxy species can be most easily prepared in acid zeolites by flowing dimethylether around 150 °C. They have been characterized using ^{13}C MAS NMR spectroscopy and IR spectroscopy. They are stable up to temperatures near 220 °C, where C-H bond dissociation starts to be observed. Below this temperature, they react with a variety of bases (Jiang et al., 2006).[12] The methoxy species react at room-temperature with ammonia to form methylamine and regenerate the Brønsted acid site. At higher-temperatures they react with toluene to form xylenes. Methoxy species will react with anhydrous HCl to form methylene chloride and regenerate the acid site. Methoxy species will also react readily with water to from methanol, and consequently, practical applications of this chemistry require anhydrous environments.

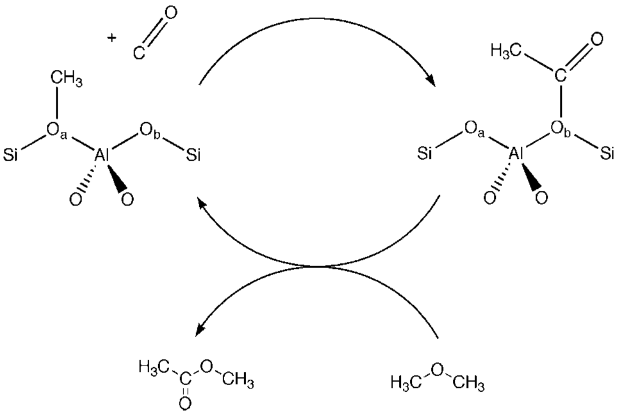

Figure 3. Reaction mechanism of carbon monoxide addition to dimethyl ether to form methyl acetate.

One especially interesting example of the reactivity of methoxy species is the catalytic synthesis of methyl acetate from dimethylether and carbon monoxide (Bhan et al., 2007; Cheung et al., 2007).[15,16] This reaction has been studied by Iglesia's group who have discovered that zeolites containing 8-rings (mordenite and ferrierite) perform this reaction faster than other zeolites. The elements of the catalytic cycle are illustrated in Figure 3. The starting point for the reaction is a zeolite already containing surface methoxy groups. The addition of carbon monoxide leads to the formation of a carbon-carbon bond and a surface acyl intermediate. It is really surprising that this rate-determining step actually occurs at reasonable rates in zeolites, since carbon monoxide is such a weak base. The second step is the reaction of the acyl intermediate with dimethyl ether to regenerate the methoxy group on the zeolite surface.

The structure of the transition state of the "methyl shift" that forms the carbon-carbon bond is not known at this time. The ability of mordenite and ferrierite to catalyze this reaction suggests that oxygen atoms opposite to the surface methoxy site (in the other side of the 8-ring) are playing a role stabilizing the transition state, but no reliable models have been reported, thus, far. This reaction is important because it is a heterogeneous alternative to the classical methylacetate synthesis using rhodium and iridium complexes. Moreover, it shows the exceptional reactivity of methoxy groups in zeolites and suggests that molecules with a stronger basicity than CO could be cajoled to react.

Other trivalent metals besides Al^{III} (B^{III}, Fe^{III}, Ga^{III}) can be readily incorporated in the zeolite framework showing similar (Fe and Ga), and lower acidity (B) than the aluminum. The structure of the catalytic sites formed by these metals is similar to the aluminum acid sites and will not be discussed further.

Hydroxyl Nests

A hydroxyl nest is a type of point defect formed in a zeolite when a silicon atom is removed from the framework (Bordiga et al., 2000).[17] A cluster of four silanol groups is left in place of the silicon atom forming a network of hydrogen bonds (see XI). These hydroxyl nests have mild acidity, and are capable of facilitating the Beckmann rearrangement of cyclohexanone oxime (XII, see Figure 4). The mechanism of this reaction has now been elucidated, and the formation of the carbenium-ion-like species XIII has been confirmed using NMR spectroscopy (Marthala et al., 2006).[18] In Figure 4, the negative charge formed on the zeolite framework is localized on a siloxy group (Si-O$^-$). In practice, because this siloxy group is part of a network of chemically equivalent groups, the negative charge is effectively delocalized between several oxygen atoms in the defect site (Fernandez et al., 2006).[19] The stability gained by this delocalization is essential for catalytic activity as high-surface area silicas with isolated silanol groups, and less organized groups of hydrogen-bonded Si-OH groups do not catalyze this reaction. Acid aluminosilicate and borosilicate zeolites do catalyze this reaction, but with much lower selectivity (Marthala et al., 2006).[18] They bind the ε-caprolactam strongly reducing the availability of the active sites for further reaction, and promoting secondary reactions, such as oligomerization of the product. The accumulation of these byproducts fills the zeolite micropores obstructing access to the active sites. Second, aluminosilicate zeolites also promote the direct desorption of the species XIII prior to the addition of water forming a cyclic imine. This byproduct is of no commercial value and decreases the economic viability of the process. Sumitomo (Izumi et al., 2007)[20] has built two plants in Asia using a siliceous zeolite (silicalite-1) containing hydroxyl nests in a fluidized-bed reactor system. The second plant with a 60,000 ton/year capacity has been working continuously since 2003. Compared to the classical process for the Beckmann rearrangement reaction using sulfuric acid, this process is superior because it uses stable and selective heterogeneous catalysts and eliminates sulfate salt byproducts, an unavoid-

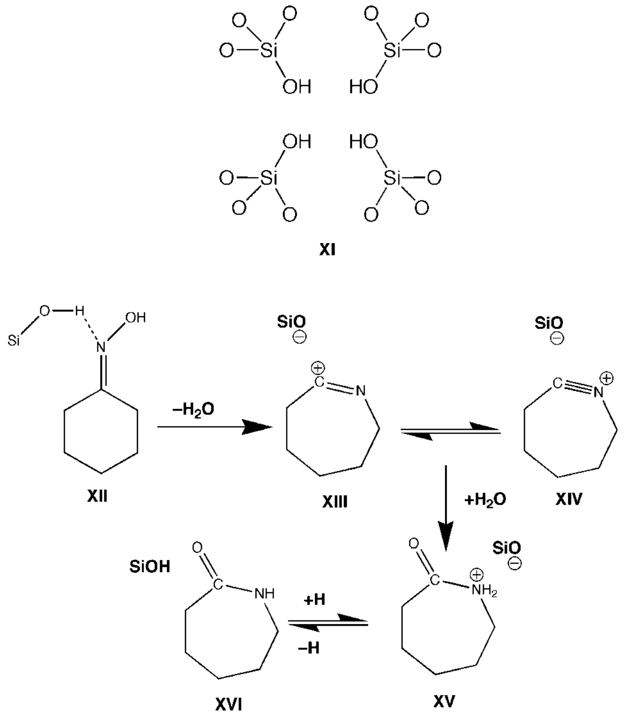

Figure 4. Structure of a hydroxyl nest defect formed on a zeolite framework (XI), and the Beckmann rearrangement mechanism of cyclohexanone oxyme (XII-XVI) on these sites.

Table 1. Comparison of the Structural Properties of Tetravalent Metals in Zeolite Frameworks

	Si	Ti	Zr	Sn
r(M-O), Å	1.62	1.79	1.96	1.88
Electronic Structure	–	d^0	d^0	d^{10}
Coordination environment in MO_2 (solid)	4, tetrahedral	6, octahedral	8, cubic	6, octahedral

(Boronat et al., 2006).[21]

able consequence of the neutralization of the mineral acid catalyst.

Lewis Acid Sites

One of today's pressing issues in heterogeneous catalysis is the development of effective solid Lewis acids that can substitute for conventional Lewis acids ($AlCl_3$, $ZnCl_2$, etc.) (Corma and Garcia, 2003).[22] Conventional Lewis acids suffer from a series of draw backs including the need for nearly stoichiometric quantities of the Lewis acid, the need for complete decomposition of the Lewis acid after reaction to recover the product (with a concomitant large byproduct stream yielding kilograms of byproduct per kilogram of product), and the use of special solvents. Solid Lewis acids stable to air and moisture that can be separated from the reaction mixture, and reused without complex pretreatment procedures have been sought by many groups. Progress has recently been made by the incorporation of isolated tetravalent metal atoms (Ti^{IV}, Sn^{IV} and Zr^{IV}) (Boronat et al., 2007; Zhu et al., 2004)[23,24] into siliceous zeolite frameworks, and new reports indicate that these materials can indeed be used for a variety of Lewis-acid-catalyzed reactions.

A Lewis acid is an electron pair acceptor and Lewis acids facilitate chemical reactions by forming an adduct between the Lewis acid, and one of the reactants (a base). This complex activates the molecule toward further reaction with other molecules in the reaction medium. On its surface, the transformation of a siliceous framework into an effective Lewis acid catalyst is a difficult proposition. Molecules adsorbed in a zeolite pore do not have physical access to the Si^{IV} metal atom in the center of tetrahedron because the short Si-O bond length ($\sim$1.62 Å), and the inflexibility of the [SiO_4] tetrahedron. Success has been achieved by the incorporation of tetravalent metals with larger cationic radii than silicon, and with the ability to have a flexible geometry and coordination number (Boronat et al., 2006).[21] Table 1 compares the M-O bond lengths, electronic structure and coordination environment for Ti^{IV}, Sn^{IV} and Zr^{IV}. The three metals have radii larger than silicon, allowing for direct bonding of adsorbents to the metal cation. One important difference between tin and zirconium is that tin is a d^{10} metal, and zirconium is d^0 and, consequently, the lowest unoccupied molecular orbitals (LUMO) are of *sp*-type in tin and d^{z^2} type in Zr. Experimental and computational studies also indicate that Ti and Sn are present in the zeolite in two coordination environments (Figure 5). Computational studies also suggest that for Ti and Sn the structure tricoordinated to the zeolite framework (XVIII) is the most active of the two (Boronat et al., 2006).[25] Similar studies have not been conducted on Zr-containing zeolites, but it is likely that its coordination is similar. Which of the two types of coordination is most abundant depends on the sample history and reaction conditions.

Titanium-containing zeolites (TS-1 and others) were the first to be synthesized and investigated in detail. TS-1, for instance, can catalyze alkane oxidations, olefin epoxidations, cyclohexanone ammoximation, etc. (Boronat et al., 2006).[25] The mechanism of epoxidation appears to proceed through proximal oxygen abstraction (Figure 5), where the need for coordination to the metal to activate the hydrogen peroxide is evident (Wells et al., 2006).[26] The mechanism of other oxidations remains a matter of debate.

Zr- and Sn-based catalysts are also active in oxidations using hydrogen peroxide, but surprisingly they are inactive toward epoxidations similar to the one depicted in Figure 5. They are, however, very active for other types of oxidations. One of them is the Baeyer-Villiger oxidation (Figure 5), where a ketone is transformed into a lactone. This diagram shows that in this reaction the metal prefers to bind to the ketone rather than to the peroxide, and this difference may explain some of the differences in reactivity between the Ti-containing materials, and the Sn- and Zr-samples. The investigation of the catalytic properties of these Lewis acids is an emerging and promising area of study. Very recently, Corma and collaborators have shown that Sn-zeolite beta is an excellent catalyst for the formation of asymmetric ethers (Corma

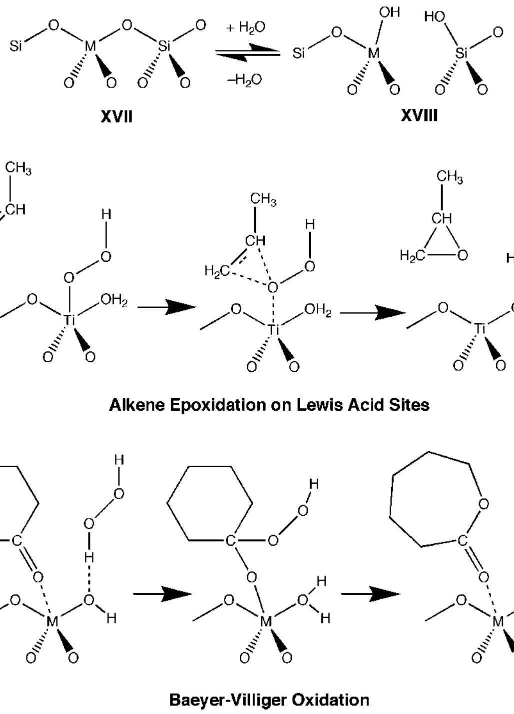

Figure 5. Coordination of Lewis acid sites (M^{IV}) in the zeolite framework, and two examples of selective oxidations using hydrogen peroxide as oxidant.

and Renz, 2007),[27] important intermediates in the pharmaceutical and perfume industries. Lewis acid catalysis is a vast area, and there are certainly many reactions in which these new materials can prove useful. We need to develop experimental/theoretical strategies that help the identifications of the promising niches. Novel approaches are essential, because the small-scale operations of the fine chemical industry do not allow, for economic reasons, for much investment in the development of new processes.

Fe-ZSM-5 Oxidation Catalyst

It is possible to incorporate metal centers in extra-framework positions (Cu^+, Cu^{2+}, Ni^{2+}, etc.) by ion exchange or gas-phase treatments, and here we want to focus on the specific case of Fe-ZSM-5 materials. These are active in a series of interesting oxidation reactions and have been studied extensively (Hansen et al., 2007; Zecchina et al., 2007).[28,29] These catalysts are active in the following reactions:

1. N_2O decomposition: $2N_2O \rightarrow 2N_2 + O_2$
2. N_2O reduction by CO: $N_2O + CO \rightarrow N_2 + CO_2$
3. Hydroxylation of benzene to phenol: $C_6H_6 + N_2O \rightarrow C_6H_5OH + N_2$
4. Oxidation of methane: $CH_4 + N_2O \rightarrow CH_3OH + N_2$
5. and others, such as selective catalytic reduction of NOx by ammonia and hydrocarbons.

Despite extensive investigations, debate remains about the structure and nuclearity of the active site (mononuclear vs. binuclear), and here I can only provide a brief overview of the salient features of the chemistry of these materials. Fe-ZSM-5 catalysts are prepared by starting with H-ZSM-5 (containing $[AlO_4]$ H^+ units in the framework), and treating the sample with a source of mononuclear iron (using solution or gas-phase methods). This treatment forms a material with iron species in the zeolite pores, but also in the exterior of the crystal. After the ion exchange, the samples are first calcined at high-temperatures (usually above 500°C), and then heated *in vacuo* or inert atmosphere to temperatures above 500°C. This activation procedure leads to oxidation/reduction of the iron species, and in most cases to clustering and aggregation of the iron species forming iron oxyhydroxides inside and outside the zeolite micropores. Despite the tendency to aggregation of the iron, a fraction of the iron atoms remains isolated in the sample, and is reduced from Fe^{3+} to Fe^{2+} during the activation procedure (Zecchina et al., 2007).[29] There is wide agreement that the active species is associated with the Fe^{2+}. The fraction of the iron in the Fe^{2+} state depends on the preparation procedures and the details of the activation, but in all active materials a fraction of the iron is left as highly undercoordinated Fe^{2+} cations. The iron oxide formed from aggregation of iron species is catalytically inactive. It is presumed that the undercoordinated Fe^{2+} cations are responsible for the observed activity. However, the coordination environment of these cations (whether is mononuclear, associated with $[AlO_4]^+$ sites, etc.) is unknown.

Carbide Nanoparticles in Zeolite Pores

It is possible to form small metal-carbide nanoparticles in zeolites by carburizing a metal oxide precursor highly dispersed in the zeolite pores. Molybdenum (Ding et al., 2001; Kim et al., 2000),[30,31] tungsten and vanadium carbide nanoparticles have been prepared in zeolite ZSM-5, and could in principle be prepared in many other zeolites as well. Generally a volatile solid precursor (such as MoO_3) is mixed with the zeolite, and the mixture is heated until the precursor diffuses into the zeolite pores, and reacts with the acid sites of the zeolite (Kim et al., 2000).[31]

The role of the zeolite is to stabilize this highly disperse form of dinuclear Mo precursors $(Mo_2O_5)^{2+}$, which then can react with a hydrocarbon (CH_4, C_2H_4) to form small MoC_x clusters of about 1 nm in size. The zeolite pores offer an environment that sterically hinders the clusters from growing any further. In particular, zeolite ZSM-5 has pore intersections with an effective diameter ($\sim$1 nm), larger than the pore windows ($\sim$0.5 nm) freezing in place the carbide particles as they are formed. Structural and reaction studies of the MoC_x clusters in ZSM-5 indicate that $x \sim 0.5$, and that the clusters have approximately the structure of Mo_2C (Lacheen and Iglesia, 2005).[32]

Samples containing the carbide clusters are active for the aromatization of methane to form benzene, naphthalene and other aromatic hydrocarbons at temperatures above 700°C. This reaction is limited by thermodynamic equilibrium to about 14% conversion at 700°C, and materials have been found that can achieve close to equilibrium conversion. The unusual catalytic properties of MoC_x/ZSM-5 materials have led to extensive study of this and related systems by various groups (Solymosi and Szechenyi, 2004).[33] It is generally accepted that the catalysts is bifunctional. The carbide nanoparticles break the C-H bond of methane leading to the formation of C2 hydrocarbons. The C2 hydrocarbons can desorb from the particles and react on other sites, where they form benzene and other species. What is the structure of the other sites? It was originally suggested that the Brønsted acid sites are regenerated upon carburization of the metal oxide precursors, and that these acid sites could trimerize and dehydrogenate the cyclic hydrocarbons to form aromatics. However, Solymosi et al. have shown that in fact the Brønsted acid sites are not reformed on carburization (Ovari and Solymosi, 2004).[34] Recently, we have reported that above 600°C Brønsted acid sites decompose by dehydrogenation (Nash et al., 2008).[35] The structure of the site after the dehydrogenation step is at this time not known. Quantum chemical calculations and studies of Al sites in quartz suggest that $[AlO_4]^0$ sites are formed (To et al., 2005).[36] These are sites where one oxygen atom has been oxidated to a formal oxidation state of 1-, further suggesting that the dehydrogenation of C2 hydrocarbons can occur through surface-radical species, and not through carbenium-ion-like intermediates. Unfortunately direct evidence for $[AlO_4]^0$ sites in the zeolites is lacking.

There is ample opportunity for further study of the formation, stability and catalytic activity of metal carbide nanoparticles in zeolites. The ZSM-5 zeolite has been studied with great detail, but other potentially interesting zeolite supports, such as beta, have not been studied in any depth. In particular, tungsten carbides should receive more attention since these carbides are more thermally stable than their molybdenum counterparts and catalyze similar reactions (Zellner and Chen, 2005).[37] Higher-temperatures are needed to increase the conversion to more industrially attractive values.

Final Remarks

In this perspective we have described some of the types of catalytic sites that can be prepared in the pores of zeolites. Many other interesting examples have not been included because of space limitations. Not discussed here is the fact that the same site on different zeolite frameworks can give rise to different selectivity depending of the size of the intermediates and activated complexes. Although catalysis with the classical Brønstead acid site of zeolites is now a mature field, catalysis with other types of sites remains largely unexplored. Even with Brønsted acid sites, our better understanding of the reaction mechanisms of these materials can suggest new temperature and pressure windows, where new (and old) reactions could possibly be run successfully.

The variety of catalytic sites greatly increases the number of reactions that can be catalyzed by zeolitic materials. In fact, it could be said that more novel chemistry has been discovered by the development of new catalytic sites in zeolites that with the discovery of new zeolite structures. Should we expect to continue to find chemically new catalytic sites in zeolites in the future? Probably not as often as we have found, thus far, simply because there are limits to the size of the periodic table, although there may be new opportunities by changing not the metal, but the apical oxygen of the zeolite framework by, e.g., nitrogen (Narasimharao et al., 2006).[38]

Finally, it is clear that quantum chemical calculations have played a major role advancing our understanding of the molecular mechanisms of zeolite-catalyzed reactions. The improvement of the methodology used for the calculations, and the rapid increase of the available computer power indicate that the impact of computational chemistry will rapidly accelerate in the coming decade in all aspects of zeolite catalysis.

Acknowledgments

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